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X-RAY FLUORESCENCE MULTISPECTROMETER FOR RAPID ELEMENTAL ANALYSIS OF PARTICULATE POLLUTANTS

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CONTENTS

	Page
ABSTRACT	iv
LIST OF FIGURES	v
LIST OF TABLES	vi
ACKNOWLEDGMENTS	vii
INTRODUCTION	1
SUMMARY	3
CONCLUSIONS	4
GENERAL DESCRIPTION OF INSTRUMENT	5
Spectrometer Channels	5
X-ray Tubes and Power	7
Compact Electronic Channels	7
Vacuum Chamber	8
Automatic Sample Handling	8
Computer Operation and Data Processing	8
SPECTROMETERS	11
SAMPLE CONFIGURATION AND HANDLING	19
Filters and Sample Deposits	19
Sample Handling	19
Automatic Sample Loader and Retriever	20
CALIBRATION	22
INSTRUMENT OPERATION AND DATA PROCESSING	23
Instrument Control	23
Calibration, Measurement, and Data Processing	23
INSTRUMENT PERFORMANCE	25
Sensitivities and Detection Limits	25
Precision and Accuracy Estimates	26
Analyses of Source and Ambient Air Samples	29
REFERENCES	32

ABSTRACT

A multichannel wavelength x-ray fluorescence spectrometer, specially adapted for rapid analysis of air pollution particulate samples, is described. The system contains an array of fixed-wavelength spectrometers optimized for simultaneous analysis of 16 preselected elements and a computer-operated scanning channel for the determination of any number of additional elements. A loading device permits automatic handling of batches of up to 100 frame-mounted 47 mm filter samples. Instrument operation, data processing, and printout of results are controlled by a minicomputer. The system permits rapid elemental analysis at high spectral resolution, a significant advantage with air pollution samples which typically contain several dozen elements at a wide range of concentrations. For samples deposited on membrane filters, detection limits for 100-second counting times are in the range of 2 to 40 ng/cm^2 for most elements of interest.

LIST OF FIGURES

Figure		Page
1	Simultaneous X-ray Multispectrometer System	6
2	Monochromators in Vacuum Chamber.	9
3	Automatic Sample Loader	10
4	Double Monochromator.	12
5	Beam Paths in a Double Monochromator.	12
6	Compact Scanning Spectrometer	13
7	Scanning Spectrometer Shown Schematically at Three Wavelength Settings.	14
8	Sequence of Views of Scanner at Eight Wavelength Settings.	15
9	Scanner Slit-to-Crystal Distance as a Function of X-ray Energy.	16
10	Comparison of X-ray Spectra Obtained with Wavelength and Energy Spectrometers on a Calcium-Potassium Sample	18
11	Separation of K Lines of Mn, Fe, and Co by the Scanning Channel.	18
12	Exploded View of a Frame-Mounted Filter	21
13	Sample Cup - Top and Side Views	21
14	Comparison of X-ray Fluorescence and Gravimetric Determinations of K_2SO_4 Deposited on Nuclepore Filters.	28

LIST OF TABLES

Table		Page
1	Fixed Monochromators in EPA Spectrometer.	7
2	Resolutions Measured with Scanning Wavelength and Energy-Dispersive Spectrometers.	17
3	EPA Multispectrometer XRF Analyzer Element Sensitivities and Detection Limits	25
4	Precision of Replicate Analyses of Potassium. . . .	26
5	Magnitude and Uniformity of Background Count for Three Types of Membrane Filters.	27
6	Comparison of XRF and AAS Analyses on Particulate Samples from a Simulated Combustion Source . . .	29
7	Typical XRF Analyses of Particulate Emissions from 1975 Catalyst-Equipped Cars	30
8	XRF Analysis of Flyash from Coal-Fired Power Plant.	30
9	XRF Analyses of Ambient Air Particulate Samples . .	31

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X-RAY FLUORESCENCE MULTISPECTROMETER FOR RAPID ELEMENTAL ANALYSIS OF PARTICULATE POLLUTANTS

INTRODUCTION

The chemical characterization of particulate pollutants in the environment has been greatly facilitated by the development in recent years of a number of instrumental multielement analytical procedures. The four techniques used most widely for elemental analysis of airborne particulate samples are optical emission spectroscopy, atomic absorption spectroscopy, neutron activation, and x-ray fluorescence. Each of these methods has definite advantages and disadvantages, though none is applicable to all elements.

The use of x-ray fluorescence is noticeably increasing at this time because of a number of attributes that make it especially attractive for the analysis of airborne particulate matter. These features include (1) the direct analysis of filter deposits with no need for sample preparation; (2) the non-destructiveness of the method, which permits samples to be retained for further analysis or future reference; (3) the fairly uniform detectability across the periodic table, with the ability to analyze all elements from atomic number 9 (F) upward; and (4) the availability of commercial instruments that permit the analysis of samples for a large number of elements in relatively short time intervals and at low cost.

Competition exists not only between x-ray fluorescence and other analytical methods but also within the x-ray fluorescence method itself, e.g., between wavelength dispersion and energy dispersion. Birks and his

coworkers at the Naval Research Laboratory carried out an EPA-supported laboratory study[1,2] to develop x-ray fluorescence as a method for routine multielement analysis of filter-deposited particulate samples. The study compared various x-ray fluorscence techniques, including the options available for both excitation and detection of the fluorescence. Among the main conclusions were the following:

1. The single-element limit of detection, where interferences are absent or neglible, is about the same for either wavelength or energy dispersion.

2. Atmospheric particulate samples and samples from power plants, incinerators, and other source emissions typically contain many elements at widely different concentrations. Energy-disperse x-ray fluorescence spectra for such samples show significant interferences between neighboring elements, particularly the elements from sulfur to nickel in the periodic table; and require mathematical unfolding to determine the x-ray intensities. For such real pollution samples, the use of wavelength dispersion spectrometers with their high-resolution capability is a distinct advantage; their use requires considerably less data manipulation, thus avoiding what can be in many instances a major source of error.

3. For routine analysis of large numbers of samples, in which elements of interest can be specified in advance, the use of multi-channel wavelength spectrometers appears as the most practical solution, inasmuch as these instruments combine two important features, i.e., high spectral resolving power and simultaneous measurement of a large number of elemental concentrations.

An instrument of this kind, adapted for analysis of filter-deposited samples of particulate matter, has been set up and is in routine use at the EPA Environmental Research Center in North Carolina. Its essential features and performance are described in this report.

SUMMARY

A simultaneous x-ray spectrometer, containing an array of 16 fixed monochromators and a sequential channel, has been specially adapted and equipped by the EPA for automated analysis of filter-deposited samples of particulate matter. It is being used successfully for the rapid and routine analysis of large numbers of air pollution particulate samples for 20 to 30 elements per sample.

The multichannel wavelength spectrometer is capable of carrying out simultaneous analysis of many elements in a sample, as is the case for energy dispersive units; but it has in addition two important advantages. Its crystal spectrometers can yield good detection limits, i.e., 30 nanograms per square centimeter or less for most elements of interest, in relatively short count times as compared to energy-dispersive systems that are dependent on severely count-rate-limited solid state detectors. More important, the higher resolution of the crystal spectrometers permits analyses of air pollution samples, which typically contain several dozen elements at a wide range of concentrations, to be obtained with considerably less data manipulation and therefore fewer errors in correcting for interelement interferences.

The cost of analyses carried out with the simultaneous x-ray spectrometer has been calculated based upon a 5-year amortization of the capital cost, typical operating expenses, and sample burdens well within the capacity of the instrument. Estimates range from 2 to 4 dollars per sample and as low as 10 cents per element.

CONCLUSIONS

The performance of an x-ray fluorescence multispectrometer system has shown it to be a highly effective means for rapid and routine multi-elemental analysis of large numbers of air pollution particulate samples. Rapid determinations were accomplished by simultaneous analyses with one scanning and sixteen fixed spectrometers and by the relatively short counting times possible with wavelength dispersive spectrometers.

The higher resolution obtained with crystal spectrometers compared to energy-dispersive instruments reduces the interferences that occur between elements having characteristic lines of nearly the same energy. This is especially important with environmental samples that typically contain several dozen elements, including many requiring interference corrections that are large and uncertain in low-resolution instruments. The use of crystal spectrometers with their high-resolution capability thus minimizes, and in most cases eliminates, the need for mathematical unfolding procedures that can be a significant source of error in x-ray fluorescence analysis.

The measured sensitivities and detection limits are more than adequate for most elements of environmental concern. For 30 elements of greatest interest the minimum detection limits for a counting time of 100 seconds were in the range 2 to 10 ng/cm^2 and exceeded 30 ng/cm^2 for only four of the elements.

The precision of the analysis depends on counting statistics, instrument drift, specimen variation, and operational errors. Excellent precision in the total counting procedure, including specimen handling and positioning, was found in repeatability tests. Evaluation of the uniformity of various membrane filter substrates revealed that Nuclepore was the most uniform.

Comparison of the results of x-ray fluorescence analyses with the results obtained on the same samples by gravimetric or atomic absorption analysis has verified the accuracy of the method. The analytical capability of the instrument has been demonstrated with a large variety of sample types from mobile sources that included catalyst-equipped cars, diesel engines, and aircraft; from stationary sources that included incinerators, power plants, and chemical process plants; and from ambient air sampled at various locations.

GENERAL DESCRIPTION OF INSTRUMENT

The high-resolution x-ray fluorescence multispectrometer currently in use at the EPA Environmental Sciences Research Laboratory was set up to provide a means for rapid and quantitative multielement analysis in research projects to characterize airborne particulate samples and to demonstrate its capability for processing large numbers of air pollution samples for routine monitoring purposes. An overall view of the instrument is shown in Figure 1. Based upon a newly designed Siemens (Model MRS-3) simultaneous spectrometer* adapted for use with filter-deposited samples, the instrument includes automatic sample handling and computer-controlled operation and data processing capabilities.

Spectrometer Channels - The EPA simultaneous spectrometer has been equipped with 16 fixed monochromators and 1 scanning monochromator. The fixed channels permit each element from fluorine upward in atomic number to be determined by an optimally designed monochromator, including an appropriate detector for the analyte x-ray energy, and an optimum crystal. The crystals in the fixed channels are logarithmically bent in order to achieve a constant Bragg angle over the entire surface without grinding.[3,4] A list of the elements selected for the fixed channels is shown in Table 1 along with the analyte lines, crystals, and detectors employed for each channel. This list includes the nine elements with lowest atomic numbers that can be analyzed (i.e., F, Na, Mg, Al, Si, P, S, Cl, K) plus seven additional elements (i.e., Cr, Mn, As, Br, Cd, Hg, Pb).

The EPA instrument is also equipped with a fully focusing curved-crystal[5] scanning spectrometer which greatly increases the flexibility of operation and the total number of elements which may be analyzed. Scanning is accomplished by a stepping motor which may be operated manually or automatically according to pre-defined scan plans which have been inserted into the minicomputer program.

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*Simultaneous x-ray multispectrometers are currently manufactured also by Applied Research Laboratories, Philips Electronic Instruments, and Rigaku Denki.

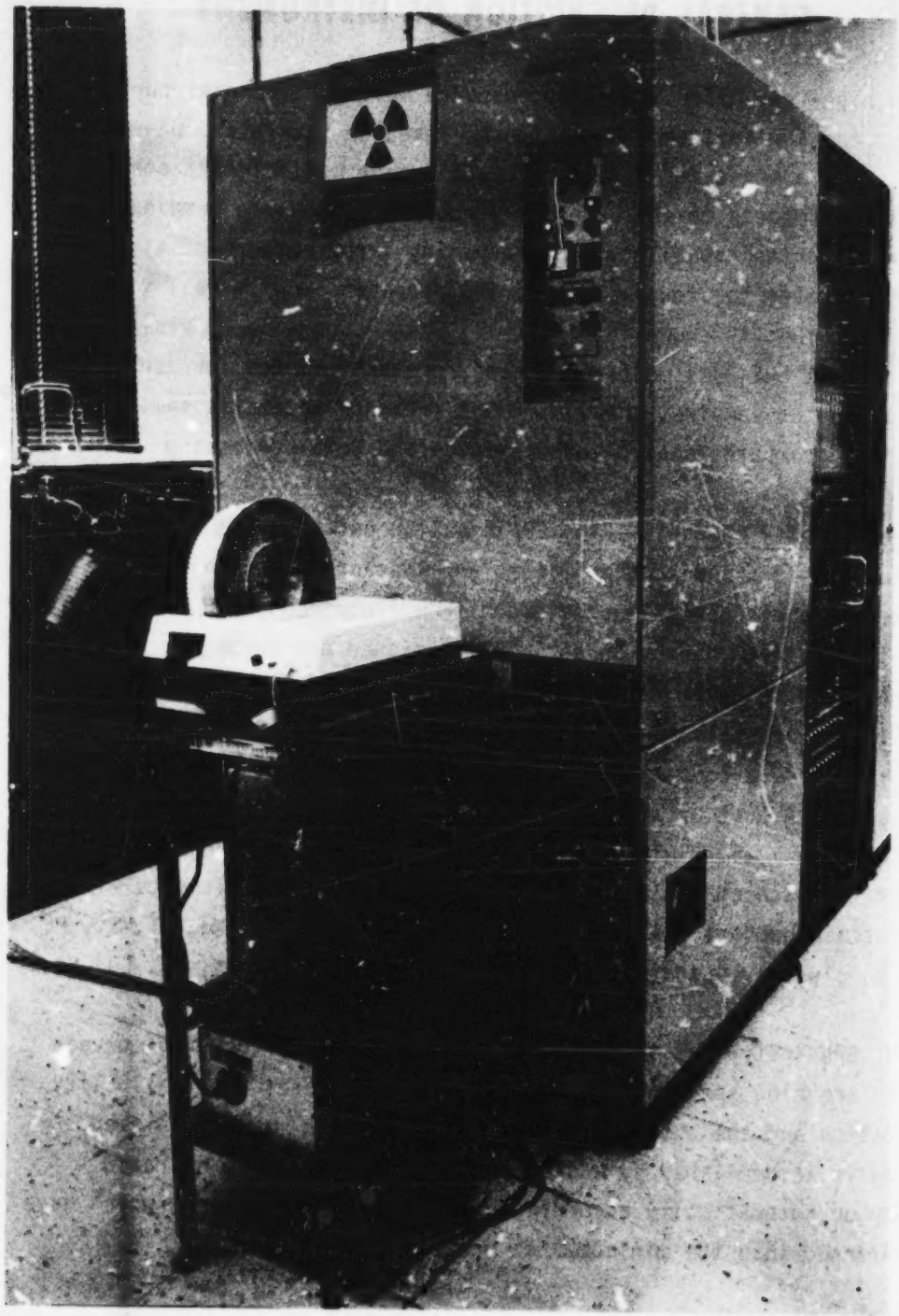

Figure 1. Simultaneous x-ray multispectrometer system.

Table 1. FIXED MONOCHROMATORS IN EPA SPECTROMETER

Electronic channel	Element	Line	Detector type	Crystal	Window thickness, μm	Spectrometer position
1	Chromium	K_α	Scintillation	LiF(200)	--	1
2	Lead	L_β	Scintillation	LiF(200)	--	1
3	Manganese	K_α	Scintillation	LiF(200)	--	2
4	Arsenic	K_β	Scintillation	LiF(200)	--	3
5	Mercury	L_α	Scintillation	LiF(200)	--	5
6	Bromine	K_α	Scintillation	LiF(200)	--	9
7	Phosphorus	K_α	Flow	PET	2	10
8	Silicon	K_α	Flow	PET	2	2
9	Cadmium	L_α	Flow	PET	6	3
10	Aluminum	K_α	Flow	PET	2	4
11	Sulfur	K_α	Flow	PET	2	5
12	Sodium	K_α	Flow	KAP	0.4	7
13	Fluorine	K_α	Flow	KAP	0.4	4
14	Magnesium	K_α	Flow	ADP	0.4	8
15	Potassium	K_α	Flow	PET	6	8
16	Chlorine	K_α	Flow	PET	6	9

X-ray Tubes and Power - Fluorescence excitation in the EPA spectrometer is accomplished by either of two interchangeable Siemens type AG61 water-cooled x-ray tubes containing chromium and rhodium targets, respectively. The high-voltage generator for the x-ray tube, which is located in the spectrometer cabinet at the opposite end from the sample changer (Figure 1), has a maximum output of 4 kW. It provides for the adjusting, reading, and stabilization of the tube voltage and current. Analyses are generally carried out using the Cr target tube, which has an output of 2600 watts at a maximum of 60 kV. When the Cr target tube is used, analyses of samples for Cr are done with automatic interposition of an aluminum filter in the primary beam.

Compact Electronic Channels - The detector amplifier signals from each of the 17 monochromators in the EPA simultaneous spectrometer are processed by a separate compact electronic NIM module. Each of the 17 compact electronic channels consists of a linear amplifier, a discriminator, and a pulse counter. There are two types of electronic modules-

one for scintillation detectors and the other for proportional flow detectors. The input pulses are processed in four three-stage amplifier sections with adjustable gain. The pulse-height discriminator allows only those pulses that lie between the upper and lower voltages of the "channel width" to arrive at the output. These pulses are counted by an eight-decade capacity counter during a given, preset time interval.

Vacuum Chamber - The characteristic x-rays of light elements are significantly reduced by absorption in air so that vacuum operation is used to analyze the lower atomic number elements. The x-ray tube, specimen holder, and array of 17 spectrometers are enclosed in a spectrometer tank (Figure 2). A vacuum control system provides a fully automatic sequence once the start button is pushed. The sample is evacuated in a forechamber; then inserted into the evacuated spectrometer tank, counted, removed from the spectrometer tank, and returned to atmospheric pressure as the vacuum is released.

The entire spectrometer tank is thermally insulated and held at a constant temperature (25°C) by water circulating through cooling tubes from a thermostat. Constant temperature is necessary since the counter tubes and the analyzer crystal lattice parameters are temperature dependent.

Automatic Sample Handling - A custom-designed automatic sample loader (Figure 3) has been fabricated to feed filter samples to the inlet port of the MRS-3 spectrometer and remove the samples after they have been analyzed. The sample loader holds up to 100 filter samples mounted in EPA-designed plastic frames. The entire sample handling process can be controlled by the programmable minicomputer so that the samples can be analyzed unattended once they have been loaded into the sample tray. Fail-safe features have been incorporated into the changer to prevent jamming.

Computer Operation and Data Processing - A Digital Equipment PDP-11/05 minicomputer with a 20K-word memory is used to control the entire spectrometer operation, including manipulation of the sample charger; insertion and removal of samples; counting of samples by the fixed-channel monochromators for programmed time intervals; programmed operation of the scanning channel for selected elements; storing of calibration and interference correction factors; and handling of output

data from all the fixed channels and the scanner. A DEC RT-11 real-time magnetic tape system is used to expand the capacity of the computer. Print-out of the results is made on a Silent 700 Texas Instrument thermal printer.

Figure 2. Monochromators in vacuum chamber.

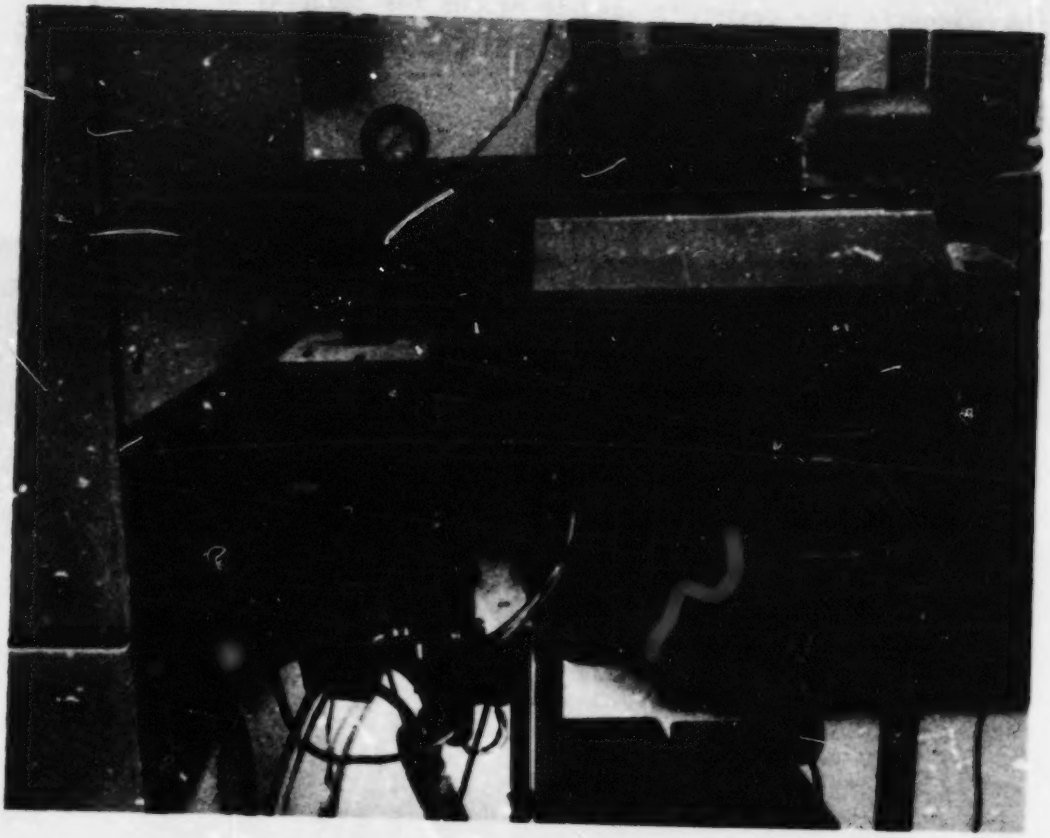

Figure 3. Automatic sample loader.

SPECTROMETERS

The EPA multispectrometer accomplishes rapid high-resolution elemental analysis of particulate samples through the simultaneous use of 16 fixed monochromators and one scanner. Each fixed channel is optimally designed for the analysis of a particular element by the proper selection of the analyte line, crystal, and detector. Table 1 lists the elements determined by the fixed channels in the EPA instrument, as well as the analyte lines, crystal, and detector used. Fixed channels for additional elements are available and can be substituted for those listed.

The monochromators are located above the specimen and opposite the x-ray tube within the vacuum-tight spectrometer housing. Arranged in a semicircle about the specimen, the monochromators are mounted at ten positions. At seven of the positions, a double monochromator is used while two single monochromators and the scanner occupy the remaining positions. A double monochromator, shown in Figure 4, is essentially two monochromators molded into one frame. As shown schematically in Figure 5 each monochromator contains an inlet slit, a logarithmically bent crystal, and an outlet slit in a focusing arrangement. Both the entrance and exit slits are adjustable in direction and width. Fine adjustment of the reflecting angle (θ) by rotation of the crystal holder and adjustment of the 2θ angle by the movement of the exit slit is possible after the monochromators are installed, the vacuum applied, and thermal equilibrium attained. This is accomplished by the attachment of a remotely controlled device to two spindles which drive gears that rotate the crystal holder and move the exit slits.

Scintillation counters are used for detection of characteristic high-energy x-rays and flow proportional counters for detection of low-energy radiation. The scintillation counters have 0.2-mm-thick beryllium windows, and the flow counters have windows of different thicknesses, i.e., 6 μm or 2 μm aluminum-coated Mylar or 0.4 μm nitrocellulose (on a support grid), according to the element being measured. For most applications, a mixture of 90 percent argon and 10 percent methane is used in the flow counter tubes.

The scanning channel (Figure 6) is a curved-crystal spectrometer adjustable over a 2θ range of 30° to 120°, and is compactly designed so that it occupies only one spectrometer position. A fully focusing spectrometer,

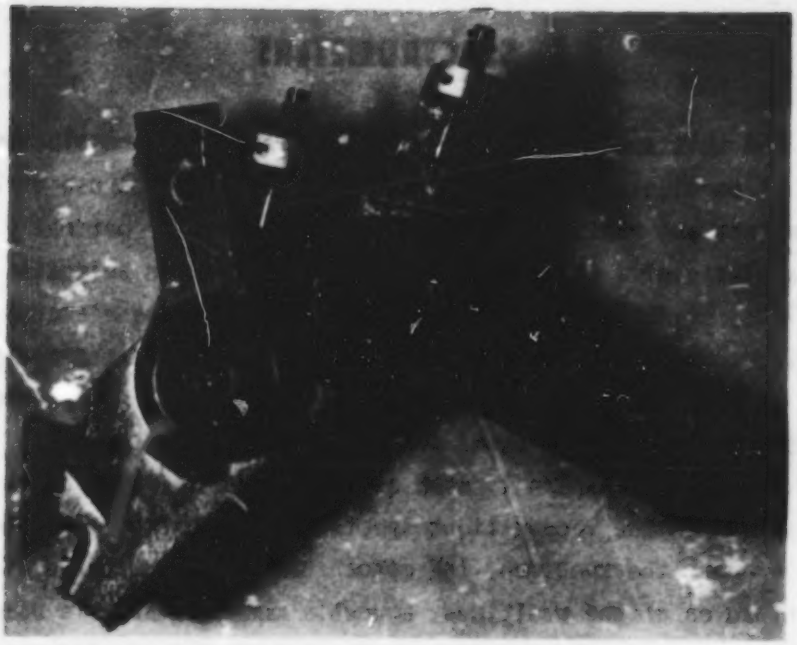

Figure 4. Double monochromator.

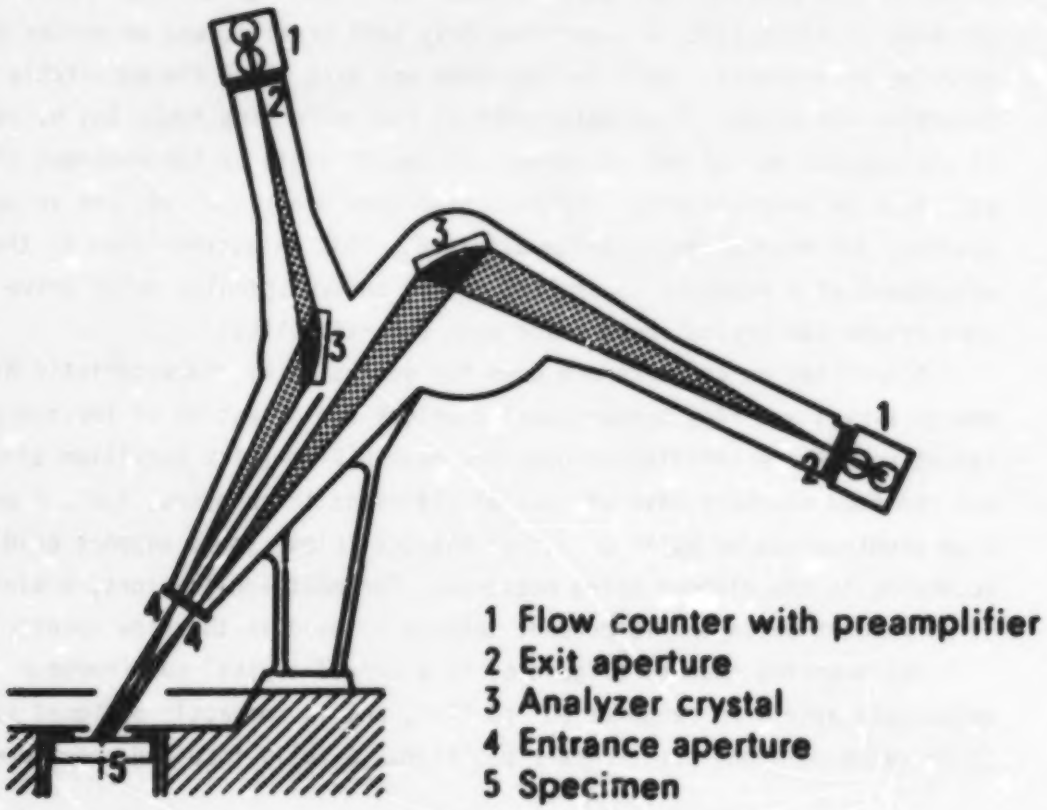

Figure 5. Beam paths in a double monochromator.

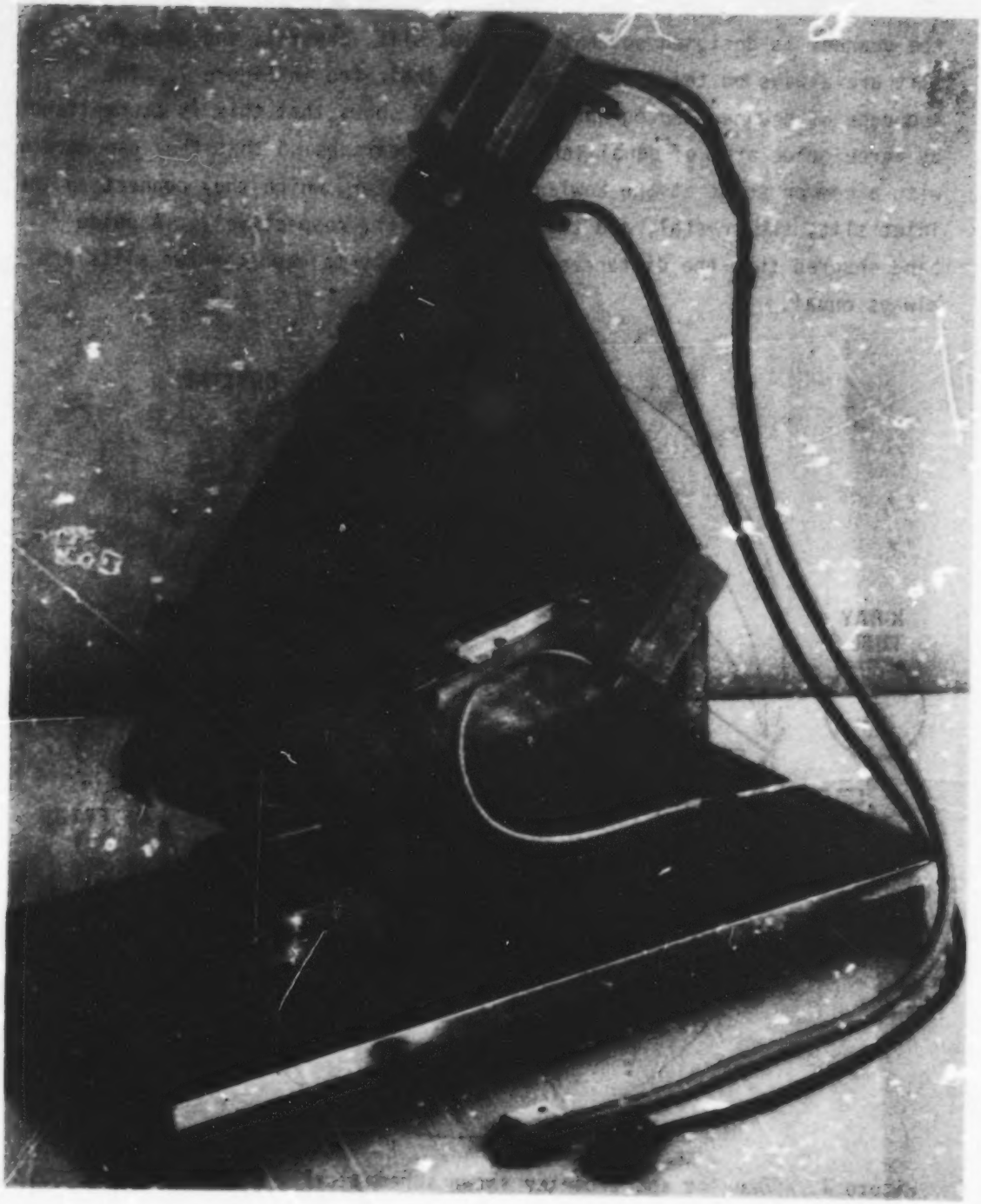

Figure 6. Compact scanning spectrometer.

the scanner is designed so that the inlet slit, crystal, and detector slit are always on the Rowland circle as indicated in Figure 7. The sequence of scanner photographs in Figure 8 shows that this is accomplished by three guide arms of equal length having bearings so that they can rotate with a common shaft at the Rowland circle center, which they connect to the inlet slit, the crystal, and the detector slit, respectively. A guide band ensures that the distances between the crystal and the two slits are always equal.

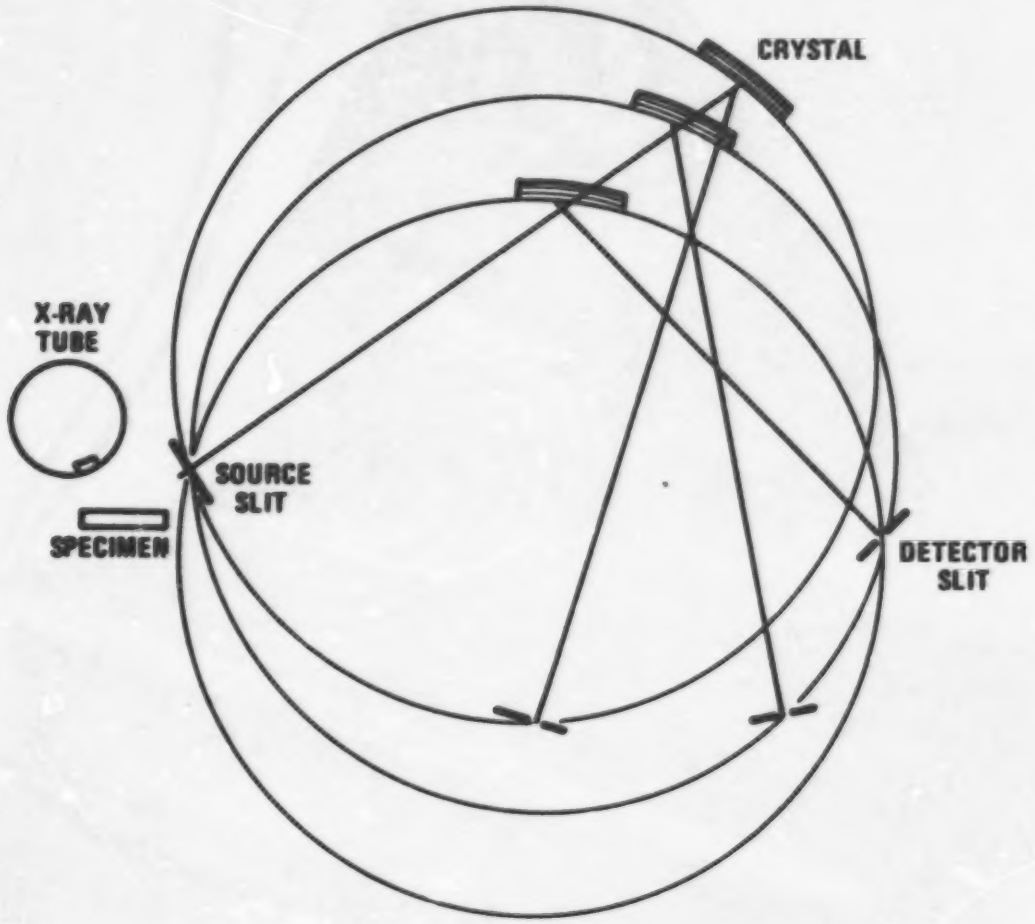

Figure 7. Scanning spectrometer shown schematically at three wavelength settings.

Since elements of atomic numbers 9 through 19 (fluorine through potassium) were included for measurement by fixed channels, the scanning spectrometer was equipped with a LiF (200) crystal, thus making it effective for analysis of all higher atomic number elements. Figure 9 shows the analytical range

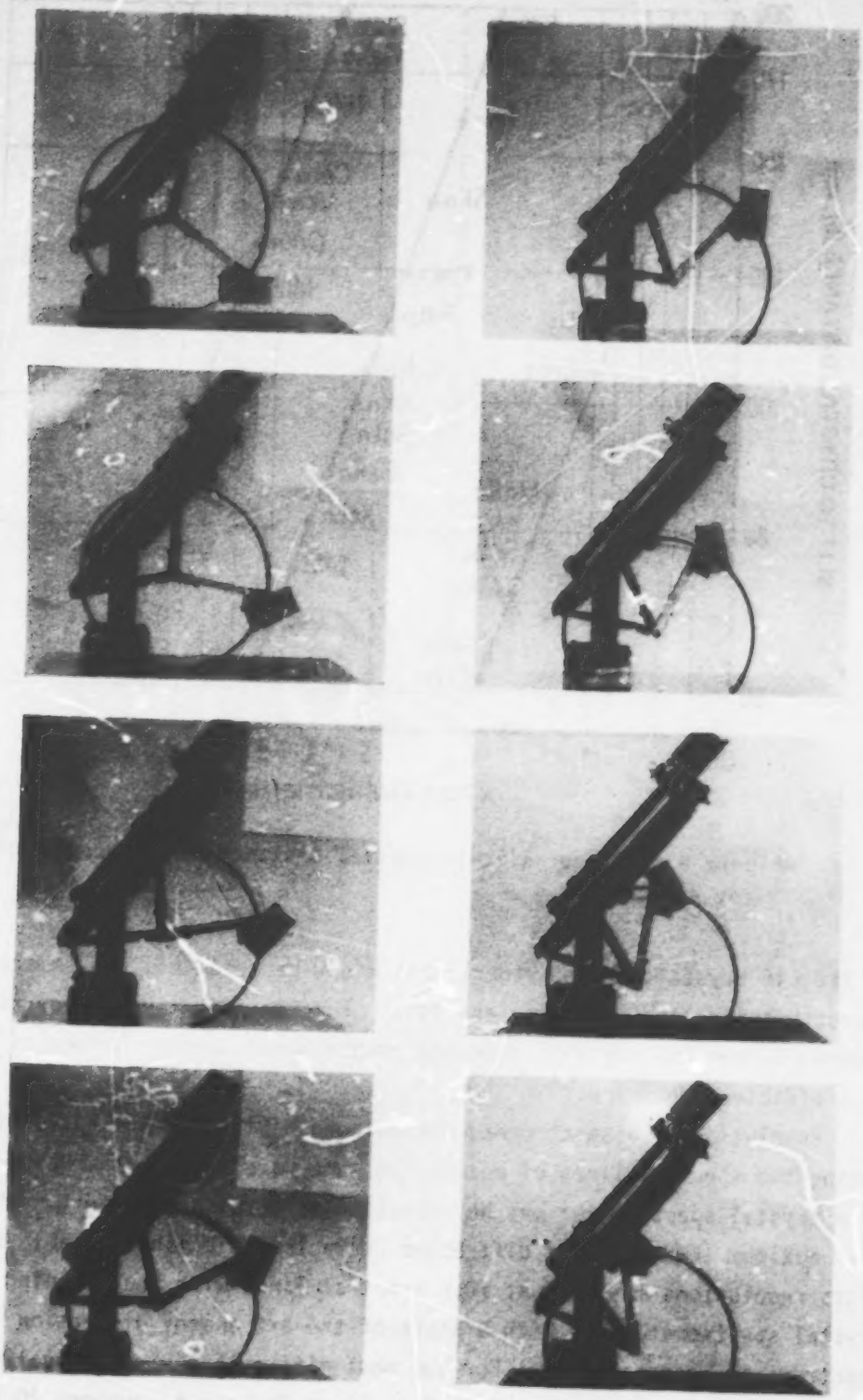

Figure 8. Sequence of views of scanner at eight wavelength settings (the Rowland circle was sketched on the photographs to show its shift with wavelength).

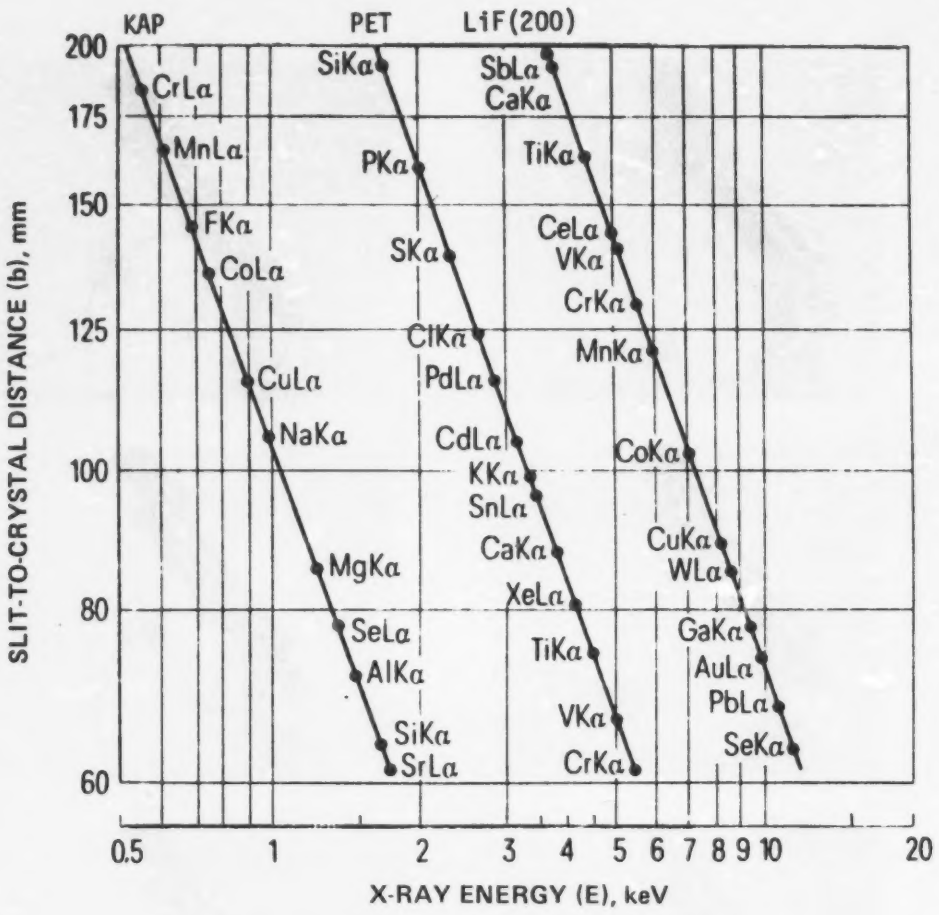

Figure 9. Scanner slit-to-crystal distance as a function of x-ray energy.

of the LiF crystal, and of others that might be selected, and some of the characteristic lines used for analysis. For the effective energy range covered by the LiF crystal, a sealed proportional counter serves as the most efficient detector.

Resolution of a spectrometer is defined as its capability for separating two spectral lines of nearly the same wavelength. The resolution of a crystal spectrometer may be expressed in terms of the full width at half maximum (FWHM) of the diffracted characteristic lines. Table 2 lists resolutions measured at four spectral lines with the scanning LiF crystal spectrometer and with a state-of-the-art energy dispersion spectrometer, respectively. For the most difficult series of analyte lines to separate, i.e., the K_α and K_β lines for atomic numbers 20 through 30 (Ca to Zn), the EPA scanning crystal spectrometer has a resolution

Table 2. RESOLUTIONS MEASURED WITH SCANNING WAVELENGTH AND ENERGY DISPERSIVE SPECTROMETERS

Element line	2θ, deg	Energy, keV	Resolution, FWHM		
			LiF (200) crystal spectrometer		Energy dispersive[a] spectrometer
			Δθ, deg	ΔE, eV	ΔE, eV
Pb L_α	33.93	10.55	0.26	154	185
Zn K_α	41.78	8.63	0.22	87	170
Mn K_α	62.97	5.90	0.20	33	155
Ca K_α	113.09	3.69	0.19	6	125

[a]Princeton Gamma-Tech Model PGT-1000.

capability from two- to twentyfold greater than that of the energy-dispersive solid state detector. Figure 10 compares the spectrum obtained for a $CaCl_2$-KCl mixture by the scanning channel with that obtained on the same sample by the energy-dispersive spectrometer. The Kβ potassium line, which is easily separated by the scanning channel, is evident in the energy-dispersive spectrum only as a slight distortion in the right side of the calcium Kα peak. The resolution that can be achieved by the scanner for the K lines of Mn, Fe, and Co is shown in Figure 11.

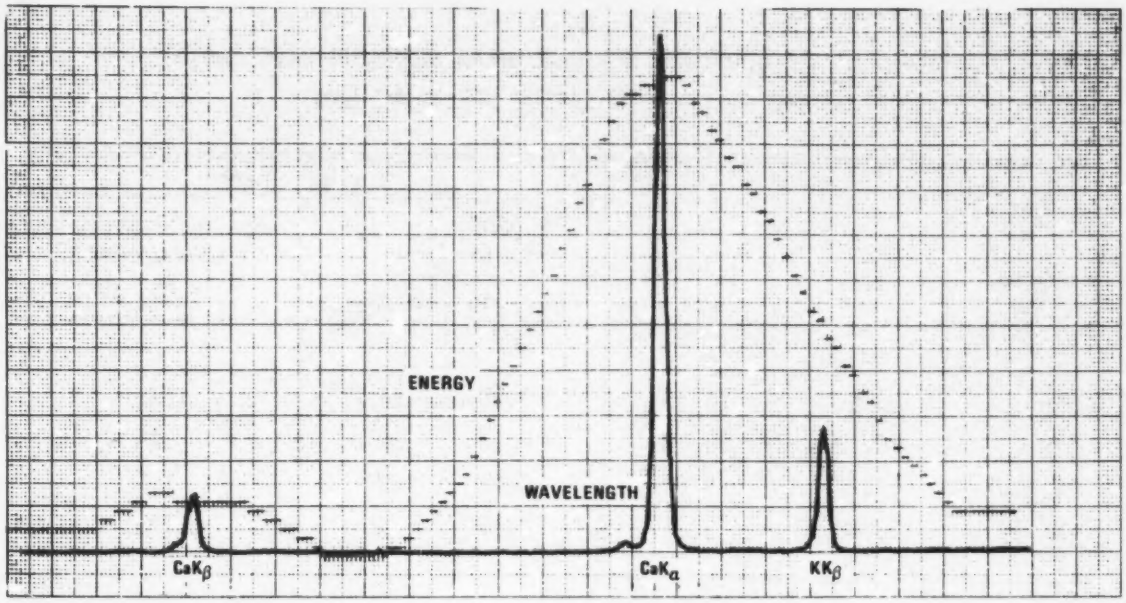

Figure 10. Comparison of x-ray spectra obtained with energy and wavelength spectrometers on a calcium-potassium sample.

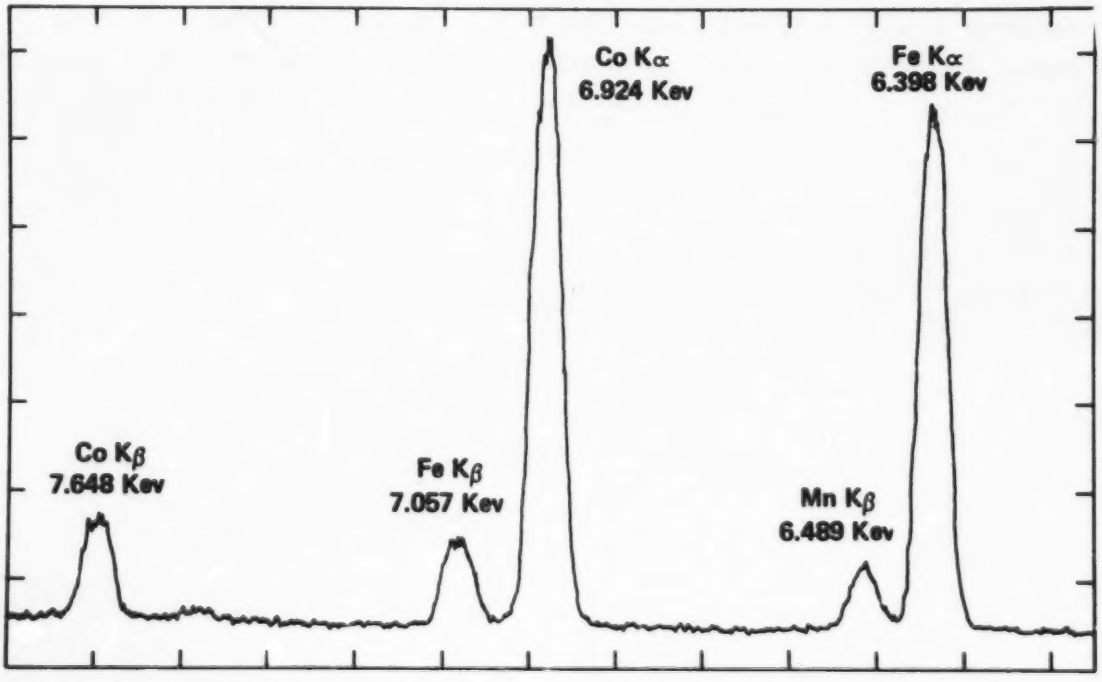

Figure 11. Separation of K lines of Mn, Fe, and Co by the scanning channel.

SAMPLE CONFIGURATION AND HANDLING

Filters and Sample Deposits - Filters used to collect air pollution particulate samples for x-ray analysis should have the following characteristics: (a) low mass to reduce scattering of incident radiation, hence minimizing the background count; (b) low content of the elements to be measured; and (c) minimal penetration of particles below the surface. Also, filters composed of low atomic number elements are desirable since these, in general, have lower attenuation coefficients and therefore lower absorption effects when penetration of the aerosol into the filter occurs. Filter materials which have been found most suitable for x-ray fluorescence analysis are the thin membrane types, e.g., Millipore, Fluoropore, and Nuclepore.

It is advantageous to use thin aerosol deposits for x-ray fluorescence analysis, inasmuch as matrix effects requiring corrections for attenuation and enhancement are thereby greatly reduced. the degree to which the matrix problem is eliminated depends on the element to be analyzed. In general, thinner samples are required for the lower atomic number elements. The criterion for a sufficiently thin sample as suggested by Rhodes[6] is:

$$m < \frac{0.1}{\bar{\mu}}$$

where m is mass deposit density in g/cm^2 and $\bar{\mu}$ is the mean mass attenuation coefficient in cm^2/g. In a matrix of typical flyash composition, analyses for sulfur (K_α) and iron (K_α) would require deposit densities not exceeding about 80 and 1200 $\mu g/cm^2$, respectively. However, fluorine, which has a $\bar{\mu}$ value in the same matrix of about 9000 cm^2/g, would require a total deposit of approximately 10 $\mu g/cm^2$ or less to meet the thin-film criterion. When multielemental analyses are to be carried out, it is obvious that compromises will have to be made in selecting optimal deposit densities, and matrix correction factors will often be required for the lighter elements.

Sample Handling - To facilitate the processing of sample deposits in the multichannel analyzer, special two-piece plastic frame mounts

were designed for 47-mm filters (Figure 12). The mounts consist of a lower ring with a 50-mm outer diameter and 32-mm inner diameter, and an expansible upper ring of slightly smaller outer diameter. The lower ring has a lip around the outer edge which holds the filter in place and retains the upper ring. The filter is placed in the lower ring with the deposit side up; the upper ring is contracted with snap ring pliers (which fit into two holes); it is then placed over the filter and allowed to expand into the beveled edge of the lower ring.

When the sample is inserted into the specimen area of the spectrometer, it is pressed against the underside of a gold-plated aperture plate that has a 30-mm diameter opening. This corresponds to the maximum sample deposit area exposed to primary x-ray excitation from the tube.

Frame-mounted filter samples are transported from the external sample loader into the vacuum tank of the spectrometer while seated atop specially designed sample cups, as shown in Figure 13. The sample cup serves as a trap for the primary beam that penetrates the sample and is gold-plated to reduce the quantity of backscattered x-rays.

Automatic Sample Loader and Retriever - A custom-designed sample changing system has been fabricated for automatic loading of samples mounted in the EPA filter frames. The sample changer, shown in Figure 3, holds up to 100 specimens which slide sequentially down a chute and are centered directly under one of three pick-up discs along the periphery of a large circular table that turns in a programmed sequence. Each pick-up disc has small vacuum tips of soft rubber which contact and hold the plastic sample frame at three points near its outer edge. The table then rotates 120° so that the sample is directly over a sample cup located at one of four positions in a rotating carousel. The vacuum is released as the sample is pressed into a recess at the top of the cup. The rotating carousel transports the cup with sample into the forechamber, which is then evacuated before the specimen is inserted into the spectrometer tank. At the conclusion of the fluorescence measurements, the specimen is returned to the forechamber and the vacuum released, the rotating carousel transports the sample and cup out of the instrument, where the sample is finally removed by one of the pick-up discs in the automatic sample changer. The automatic changer has a fail-safe feature that prevents jamming by terminating the entire counting procedure if a sample fails to be retrieved.

The automatic changer may be operated manually but is normally controlled by the minicomputer program.

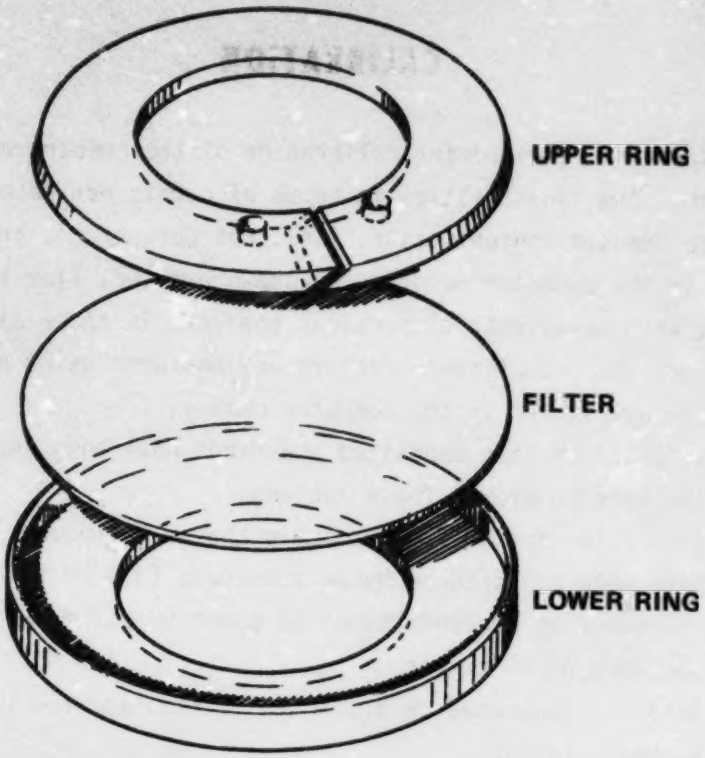

Figure 12. Exploded view of a frame-mounted filter.

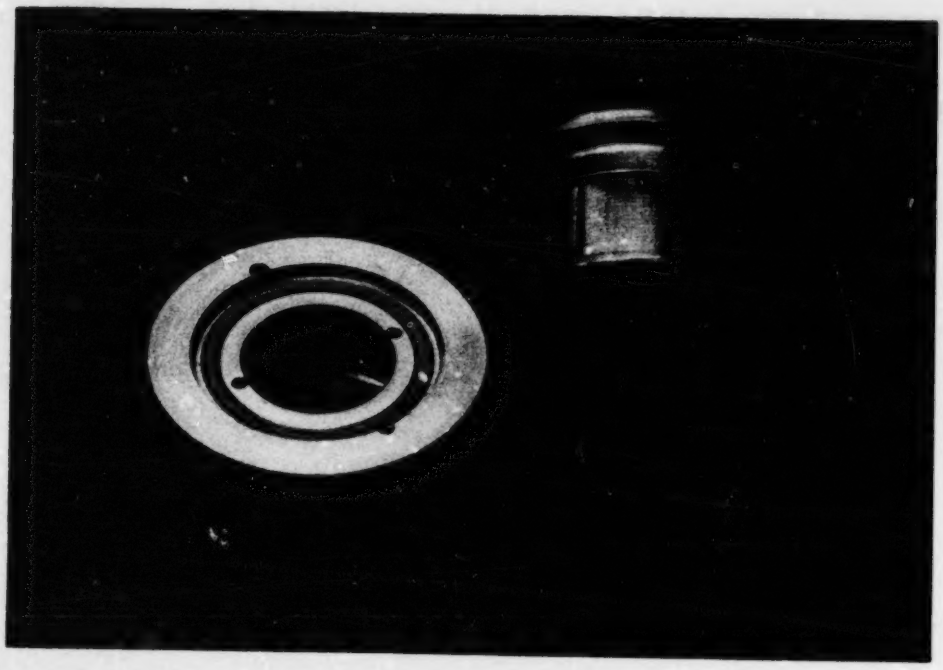

Figure 13. Sample cup - top and side views.

CALIBRATION

Standards are required for calibration of the spectrometer for each element. The sensitivities in terms of counts per second per unit surface deposit concentration, i.e., cps per $\mu g/cm^2$, are determined and stored in the computer memory. As shown earlier, line interferences are minimal with wavelength dispersion; however, in those cases where they do occur, the interference factors are measured using pure standard specimens and are stored in the computer memory.

Several types of thin deposited standards have been employed to calibrate the spectrometer. These include:

1. Thin films formed from vacuum-evaporated elements and compounds. These were prepared on Mylar substrate (3.8-μm thickness) by Micromatter Company at concentrations of about 50 $\mu g/cm^2$ with an estimated accuracy of 5 percent.

2. Aerosols generated, e.g., in a Collison atomizer, and collected on membrane filters.

3. Filter deposits of materials from solutions after solvent evaporation. This method is subject to non-uniform deposits caused by migration of ions during evaporation unless precautions are taken.

4. Filter deposits of fine powdered materials from liquid suspension.

INSTRUMENT OPERATION AND DATA PROCESSING

A minicomputer, interfaced with the multichannel spectrometer, provides automatic operation of the instrument including sample changer operation, sample transport, and control of counting parameters (selection of elements, counting time, etc.) for both fixed and sequential channels. The computer also provides data processing after the calibration and analyte specimens have been counted. The computer is a Digital Equipment PDP-11/05 unit with 20K-word memory. It has been interfaced with a Digital Equipment tape control and transport operated by a RT-11 real-time software system which expands the memory capacity and permits additional data processing to be applied as needed.

Instrument Control - Operation of the fixed channels is controlled by the selection of any one of a number of possible programs hardwired on program cards. These permit the simultaneous analysis of up to 16 selected elements for any desired counting time interval. As counting in the fixed channels begins, operation of the scanner also proceeds automatically as a result of the selection of one of several scan plans which have previously been defined and stored in the computer memory. A given scan plan contains the elements to be determined on the sequential channel and the counting time interval for each. The program also allows the operator the option of selecting a maximum count (e.g., 10,000) for each element to reduce the total count time when one or more elements are present at high concentration. In this option, the x-ray intensity from each element is measured automatically for either the designated time interval or the maximum count, whichever occurs first.

Calibration, Measurement, and Data Processing - Before elemental concentrations in particulate samples can be determined, a set of calibration standards must be inserted and processed in the instrument. The computer-controlled calibration program includes measurement of standards at the analyte lines and at other lines at which the material in the standard may interfere. Sensitivity factors for all of the elements and interelement line interference ratios are calculated and stored in the computer memory.

Analysis of a series of particulate samples on a given filter substrate is preceded by measurement of a corresponding filter blank for automatic determination and storage of background count levels and minimum detection limits for each of the elements selected for measurement. Following measurement of each particulate sample, the computer program subtracts background counts, makes line interference corrections, and applies sensitivity factors to convert cps to $\mu g/cm^2$. The list of elemental concentrations for each sample is stored on magnetic tape for later reference, or is printed out at the data terminal, or both; those element concentrations that are below detection limits are noted by asterisks. The program also provides for the application of other correction factors as needed, e.g., for variations in particulate deposit area and particle size.

INSTRUMENT PERFORMANCE

Sensitivities and Detection Limits - The sensitivity of the x-ray spectrometer for a given element is defined as the rate of change in the analyte-line intensity with a change in the analyte concentration. The minimum detection limit for x-ray analysis is often defined as the concentration of analyte corresponding to a net count equal to three times the standard deviation, i.e., three times the square root of the background count. The sensitivities and detection limits for 100-second measurements on 30 elements determined in the EPA simultaneous spectrometer, using thin-film-on-Mylar calibration standards, are listed in Table 3. It is noteworthy that the minimum detection limits for only 100 seconds of count time are in the range of 2 to 10 ng/cm^2 for

Table 3. EPA MULTISPECTROMETER XRF ANALYZER ELEMENT SENSITIVITIES AND DETECTION LIMITS

Element	Sensitivity, counts/100 sec μg/cm^2	Detection limit (100 sec, 3σ), ng/cm^2	Element	Sensitivity, counts/100 sec μg/cm^2	Detection limit (100 sec, 3σ), ng/cm^2
F	220	149	Co	16540	3
Na	534	29	Ni	14504	10
Mg	10280	2	Cu	18880	43
Al	8074	3	Zn	21066	7
Si	11614	3	As	17125	10
P	13392	15	Se	22922	12
S	28013	9	Br	50340	28
Cl	25394	9	Cd	17303	2
K	121286	2	Sn	14800	2
Ca	87817	2	Sb	31100	4
Ti	85635	2	Ba	25000	7
V	18010	7	Pt	6812	20
Cr	7484	19	Au	8498	91
Mn	17522	14	Hg	5776	90
Fe	13300	18	Pb	16583	30

more than half of the elements measured including most of the low atomic number elements. The detection limit exceeds 30 ng/cm^2 for only four of these elements.

Precision and Accuracy Estimates - The precision of x-ray fluorescence analysis depends on a combination of factors, including statistical counting error, instrument drift, specimen variation, and miscellaneous operational errors. In order to evaluate the magnitude of these factors, the replicate determinations listed in Table 4 were conducted. A large accumulated count was used to minimize the relative standard deviation resulting from statistical counting error. A single sample counted in place ten times showed a relative standard deviation of only 0.05 percent, while the count for a sample introduced into the instrument ten times had a relative standard deviation of 0.10 percent. The latter demostrates the excellent repeatability of the total counting procedure, which includes specimen handling and positioning.

Table 4. PRECISION OF REPLICATE ANALYSES OF POTASSIUM[a]

	Standard deviation, σ	Relative standard deviation $\left(\frac{\sigma}{\overline{N}} \times 100\right)$, %
Statistical counting error, $\sqrt{N}$	531	0 02
Observed variation of ten replicate count on single sample in place	1539	0.05
Observed variation of ten replicate counts on a single sample inserted and removed ten times	2729	0.10

[a]Average count, $\overline{N}$: 2,820,092.

Another factor that must be considered in the overall precision of a measurement is the uniformity of the filter substrate used to collect particulate samples, since a blank filter count is used to correct for background. Table 5 lists the average background counts and standard deviations for ten blank specimens of each of three types of membrane filters frequently used. Nuclepore filters exhibited the best overall uniformity.

Table 5. MAGNITUDE AND UNIFORMITY OF BACKGROUND COUNT FOR THREE TYPES OF MEMBRANE FILTERS

	Nuclepore 0.8μ (Mass = 1.1 mg/cm^2)		Fluoropore Type FA (Mass = 2.7 mg/cm^2)		Millipore Type AA (Mass = 5.0 mg/cm^2)	
	$\bar{N}$ [a]	σ [b]	$\bar{N}$	σ	$\bar{N}$	σ
F	1.32	0.09	549.78	28.20	1.96	0.13
Na	0.22	0.06	0.15	0.05	0.28	0.05
Mg	0.64	0.08	0.75	0.10	1.43	0.16
Si	66.22	4.44	1.25	0.25	2.29	0.27
P	17.77	0.62	17.63	2.16	16.34	0.35
S	48.54	0.82	40.21	2.23	54.52	0.63
Cl	86.49	3.18	54.44	4.81	200.24	5.59
K	64.48	2.67	63.49	2.46	212.40	2.40
Ca	4.43	1.17	8.85	3.15	333.84	7.13
Ti	2.91	0.56	7.67	1.20	12.74	1.62
V	7.95	0.80	16.10	1.93	25.71	1.65
Fe	44.28	4.21	50.41	4.86	62.51	4.79
Ni	2.10	0.36	3.51	0.67	5.52	1.12
Cu	553.46	9.03	567.36	14.13	577.69	21.61
Zn	12.14	0.81	26.31	3.49	41.34	6.82
Cd	1.87	0.08	2.12	0.11	3.18	0.17
Ba	2.35	0.35	5.00	0.57	8.27	0.94

[a] $\bar{N}$ is the mean value in cps for ten blank specimens.

[b] σ is the standard deviation in background for ten blank specimens.

An estimate of the accuracy of the x-ray analytical procedure, as carried out with the simultaneous spectrometer, was determined in a comparison with gravimetric values for the mass of potassium sulfate aerosol generated in a Collison atomizer and deposited on a series of Nuclepore filters. The graph plotted in Figure 14 shows very good agreement between the x-ray and gravimetric values. Another comparison,

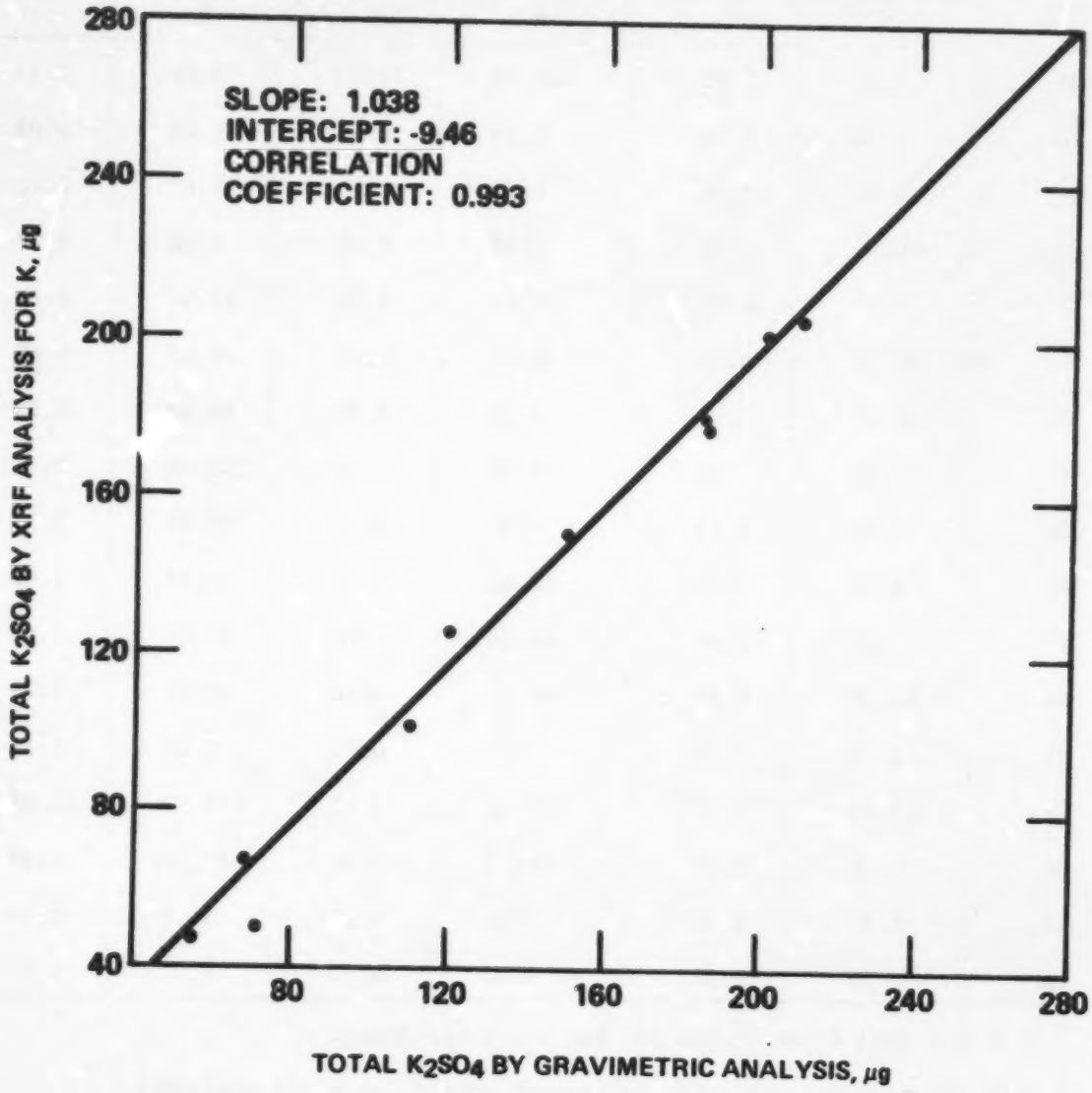

Figure 14. Comparison of x-ray fluorescence and gravimetric determinations of K_2SO_4 deposited on Nuclepore filters.

this time with atomic absorption analyses, is shown in Table 6. The samples consisted of particle emissions collected on high-purity quartz filters from a controlled combustion source fueled with oil spiked with known amounts of organometallic compounds. The calculated values shown in the table for the five metals analyzed are based upon the amount of spiked fuel consumed and the known fraction of total emissions collected on the filter. The x-ray fluorescence concentrations are in remarkably good agreement with the calculated values with the exception of the cadmium value, which is about 10 percent low, probably because of some attenuation of the relatively low-energy cadmium fluorescence resulting from only partial penetration of collected aerosol into the interstices of the quartz fiber filter.

Table 6. COMPARISON OF XRF AND AAS ANALYSES OF PARTICULATE SAMPLES FROM A SIMULATED COMBUSTION SOURCE

Element	Total collected, ug		
	Calculated value[a]	Atomic absorption	X-ray fluorescence
Pb	202	228	212
Mn	182	195	183
Co	182	193	183
Cd	183	187	166
V	216	159	230

[a] Based on analysis of fuel oil spiked with organometallic compounds.

Analyses of Source and Ambient Air Samples - The EPA simultaneous wavelength x-ray spectrometer is being used to determine the elemental composition of large numbers of samples of particulate emissions collected from mobile sources that include catalyst-equipped cars, diesel engines, and aircraft; from stationary sources that include power plants, incinerators, and chemical process plants; and from ambient air sampled at various locations. Table 7 lists elemental concentrations found in emissions from 1975 cars equipped with oxidation catalysts. The results show sulfur to be the predominant element and are in good agreement with independent measurements indicating that nearly all of the particulate matter consists of droplets of 45 percent (w/w) sulfuric acid in water. Table 8 shows typical analyses obtained from samples

Table 7. TYPICAL XRF ANALYSES OF PARTICULATE EMISSIONS FROM 1975 CATALYST-EQUIPPED CARS

Element	Concentration, $\mu g/cm^2$		
	Sample no. 4	Sample no. 8	Sample no. 30
Al	-	0.12	0.05
Si	0.40	0.02	0.11
P	0.05	-	-
S	6.80	23.00	40.50
Ca	0.08	0.08	0.04
Ti	0.02	0.01	0.01
Fe	0.32	1.10	1.40
Ni	0.02	-	0.03
Zn	0.07	0.07	0.10
Ba	0.01	-	0.02
Mass loading	46.40	143.60	270.90

Table 8. XRF ANALYSIS OF FLYASH FROM COAL-FIRED POWER PLANT

Element	Concentration, $\mu g/cm^2$		Element	Concentration, $\mu g/cm^2$	
	Sample no. X5	Sample no. X10		Sample no. X5	Sample no. X10
F	0.29	0.15	V	0.55	0.25
Na	0.42	0.35	Cr	23.	15.
Mg	2.0	1.2	Fe	20.2	9.2
Al	103.	48.	Ni	0.03	-
Si	55.	26.	Zn	4.6	0.13
P	0.54	1.0	Br	0.89	-
S	7.8	7.8	Cd	0.020	0.007
K	15.6	5.7	Ba	0.62	0.33
Ca	-	4.9	Pb	1.7	1.1
Ti	3.6	1.5			

of particulate emissions from a coal-fired power plant, and Table 9 lists element concentrations in urban air particulate samples collected at different locations and times. These data illustrate the broad range of elements and elemental concentrations present in air pollution samples.

Table 9. XRF ANALYSIS OF AMBIENT AIR PARTICULATE SAMPLES

Element	Concentration, $\mu g/cm^2$		
	Sample nos. 7-19	Sample nos. 7-24	Sample nos. 10-04
F	-	-	0.09
Na	-	-	0.09
Mg	0.02	0.06	0.14
Al	0.28	1.20	5.30
Si	0.44	1.60	7.60
P	0.11	-	0.18
S	3.74	3.20	1.77
Cl	0.26	0.15	0.47
K	0.20	0.47	2.06
Ca	1.10	0.90	2.67
Ti	0.04	0.08	0.16
V	0.005	-	0.03
Fe	0.76	0.70	2.73
Zn	1.10	0.05	0.16
Br	0.40	-	0.75
Cd	0.04	0.007	0.04
Ba	-	0.04	0.10
Pb	1.80	0.23	3.0

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